Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Materials Science 1 (2012) 608 – 613

Procedia Materials Science

www.elsevier.com/locate/procedia

11th International Congress on Metallurgy & Materials SAM/CONAMET 2011

In situ silver nanoparticles production in a polyelectrolite net recovering polyester

S. Mancini [a b] *, G. Lopez [a c], E. Calvo [b], N. Filliel [b]

[a] *Nanotek S.A – Gûemes 3878, D. 4; S3002GHH, Santa Fe, Argentina*
[b] *INQUIMAE - Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Argentina*
[c] *Facultad Regional Santa Fe - U. T. N. – Lavaise 610; S3004EWB, Santa Fe, Argentina*

Abstract

The aim of this work was to develop an antimicrobial polyester fiber by a polyelectrolyte deposition technique followed by silver nanoparticles formation in situ. Attached silver metallic nanoparticles (Ag°NPs) behave like a silver cations (Ag+) reservoir which are released to the environment when exposed to a wet medium, such as an open wound. Silver cations act against microorganisms by reacting with proteins from cellular membranes, denaturing them. This effect leads to alterations in organism growth and / or direct cellular death. Textiles were prepared by a layer by layer technique: two opposite charged polyelectrolytes, namely PAH (poly allylamine hydrochloride, positively charged) and PAA (polyacrylic acid, negatively charged), are deposited in an alternating manner in order to generate two bilayers (2PAH/PAA). Fibers are then immersed in a AgNO3 solution for a lapse adequate to allow Ag+ diffusion into the polymeric net, and subsequently they are chemicaly reduced by $NaBH_4$ to form silver nanoparticles (Ag°NPs). The amount of silver thus deposited was measured to be in the range 5.5 - 7.7 mg Ag / 100 gr fiber. These textiles were then bio-tested against Staphylococus aureus, resulting in a significant growth inhibition of biomass.

Keywords: nanoparticles; silver; nanostructures; polyelectrolites.

* Corresponding author. Tel.: +54-342-4603491
E-mail address: soniamancini79@yahoo.com.ar

2211-8128 © 2012 Published by Elsevier Ltd. Selection and/or peer-review under responsibility of SAM/CONAMET 2011, Rosario, Argentina.
Open access under CC BY-NC-ND license. doi:10.1016/j.mspro.2012.06.082

1. Introduction

Silver has been used in medicine since ancient times in several ways, such as metallic silver, silver nitrate, silver sulfadiazine, etc., for the treatment of burns, open wounds and a wide range of bacterial infections. The antimicrobial activity depends on the available silver amount in the substrate and the release rate. Metallic silver (Ag°) is inert, but it ionizes with wet skin and wound fluids. Ionized silver (Ag^{+}) is very reactive, it reacts with bacterial cellular wall and cellular membrane, inducing cellular distortion and death. Silver also reacts with bacterial DNA and RNA too, denaturalizing and inhibiting its replication [Lansdown 2006, J.J. Castellano et al 2007].

By means of nanotechnology design options of medical care products containing Agº NPs as an active component can be explored in order to enhance antimicrobial activity efficiency and to extend this effect for the useful life of the products. In this design, careful attention should be paid to the avoidance of non desirable collateral effects, such as the release of silver to the environment due to cleansing processes. Nowadays, nanometric particulate materials are being used as antimicrobial agent mainly because of their high area/volume ratio and their unique chemical and physical properties [Morones et al 2005, Kim et al 2007].

Nanoparticles are clusters of atoms with sizes between 1 and 100 nm: Silver nanoparticles can be widely used in wound treatment, in dental materials, in textile coatings, in water treatment, etc., due to their low toxicity for humans, high thermal stability and low volatility [Duran 2007]. The development of nanochemistry allows the production of very small silver nanoparticles (around 20 nm), resulting in a noticeable increase in the release of silver ions.

A wide variety of slow release silver textiles can be found in the market, which differ in silver amounts, cation release patterns and clinic applications. There is also a wide range of preparation techniques, but in general they can be classified in two main groups: *in situ* techniques (nanoparticles are formed directly inside the fibers) and *ex situ* techniques (suspended nanoparticles are first produced and modified and then deposited on the fibers).

Layer by layer technique was introduced by Decher [Decher 1997, Decher et al 1992] to produce uniform polyelectrolyte multilayers over different substrates. This technique works by absorption due to electrostatic forces arising from a charged polyelectrolyte deployed over an opposite charged surface. Because of an overcompensation charge effect, it is possible to absorb another polyelectrolyte with opposite charge. By applying this process in a sequential manner, multilayer films can be obtained, which thickness can be controlled at a molecular level by fitting different parametres, such as number of layers, pH, ionic force, etc. The nanoparticles are subsequently produced inside these nanostructured nets.

Rubner and his group at MIT [Rubner and. Shiratori, 2000] introduced the formation of metallic and semiconductive nanoparticles on polyelectrolyte multilayers, which work like nanoreactors. Later, Hinestroza`s team [Dong et al, 2008] applied a modified nanoparticle synthesis and deposition method to modify synthetic and naturals textiles.

Nomenclature

AgºNPs silver nanoparticles

2. Experimental

2.1 Textile preparation – Layer by layer technique

Fibers previously cleansed by ethanol and water were immersed in a sequential process in the polyelectrolyte solutions PAH (poly allylamine hydrochloride) positively charged and PAA (poly acrylic acid) negatively charged, for about 15 minutes in each solution. The sequence was repeated twice, thus generating two bilayers (PAH/PAA) over the polyester fibers surface. The fibers so coated were immersed in a $AgNO_3$ 20 mM solution for over 24 hours, and then reacted with $NaBH_4$ for 2 hours in order to complete the chemical reduction, by which Ag+ was converted into Ag° metallic nanoparticles.

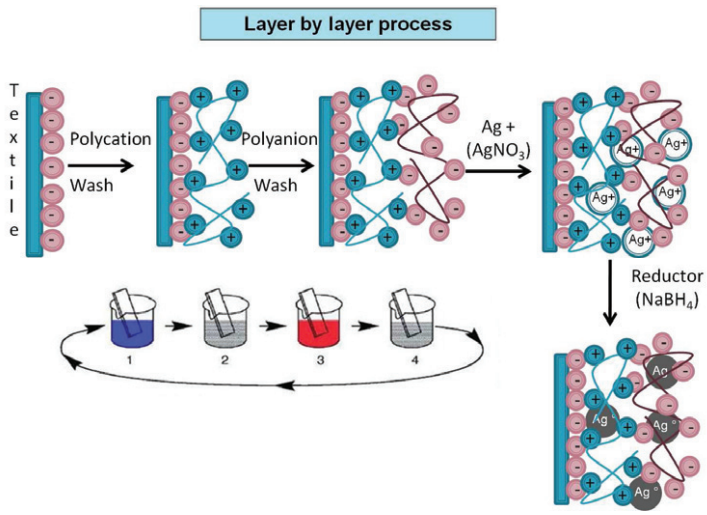

Fig. 1 – Layer by layer technique (1- Inmersion in PAH, 2 – Wash, 3- Inmersion in PAA, 4-Wash)

2.2 Electron microscopy

After fibers preparation, they were characterized by scanning electron microscopy (SEM), to determine nanoparticles size.

2.3 Atomic absorption spectroscopy

Silver amount in fiber was determined by atomic absorption spectroscopy (triplicate analysis). Samples were prepared as follows: 40 mg of fiber was pretreated with 1 ml concentrated HNO_3, for about 24 hours. The resulting solution was then diluted to 25 ml, and analytical quantification was performed.

2.4 Microbiologycal assay

Antimicrobial activity was evaluated by the standard test JIS L 1902-1998. Five 50 x 50 mm samples were prepared with NPsAg° and five without NPsAg°. They were put into individual Petri dish and then were covered completely with 400 µl of an $1x10^5$ UFC/ml *Staphylococcus aureus* culture. Petri dishes were

incubated at 37 °C and 100 % relative humidity, and samples were taken initially (time 0) and at subsequent intervals of 2, 6 and 24 hours, washed with 10 ml of 0,9 % saline solution, and diluted at a 1/100 ratio. Then 1 ml of this diluted solution was grown on a nutritive agar medium in Petri dish. Results were quantified as number of CFU (colony formation units).

3. Results and discussion

3.1 Characterization

On the SEM images (Fig. 2 and Fig. 3) it can be seen that NPsAg° were formed in the correct way within the polyester textile. They presented spherical form, 30 nm average size, and they were distributed uniformly in the surface. These results suggest that the synthesis method and the nanoparticles insertion on the polymeric matrix were successful.

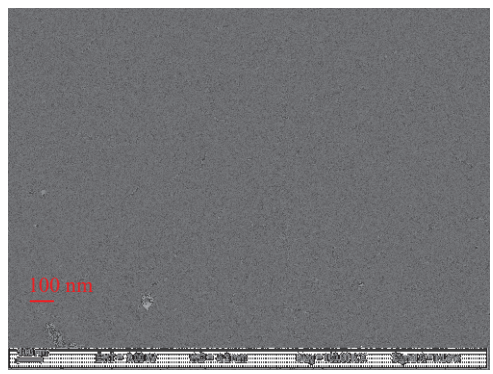

Fig. 2: Polyester fibers without Ag°NP- SEM image (CMA-UBA)

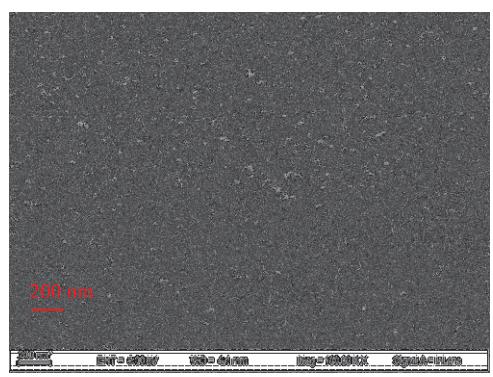

Figure 3: Polyester fibers with 30 nm average *NPsAg°* - SEM image (CMA-UBA)

3.2 Silver concentration

Results of atomic absortion spectroscopy proved that the amount of silver in the fibers ranged between 5.5 and 7.7 mg Ag^{+} / 100 gr textile (Table 1).

Table 1: Silver concentration on fibers

Assay N°	Average amount (mg Ag^{+}/100 gr fiber)	Standard Deviation
1	5.5	0.4
2	5.9	0.7
3	7.4	0.4
4	7.7	0.2

3.3 Antimicrobial activity

The antimicrobial activity against *Staphylococcus aureus* is showed in figure 4, where the evolution of the number of CFU/mL with the incubation time is plotted for different materials. The blue line corresponds to the evolution of CFU on polyester without NPsAg while the red line represents the bacteriostatic performance of polyester with NPsAg. It can be seen that the CFU/ml count increases with time for polyester without NPsAg°, indicating that bacteria proliferate continuously, while for textile with NPsAg° the number of CFU/ml remains constant in time, showing an inhibition effect on bacterial growth, quite probably due to a releasing of Ag+ from nanoparticles mechanism, as most authors agree.

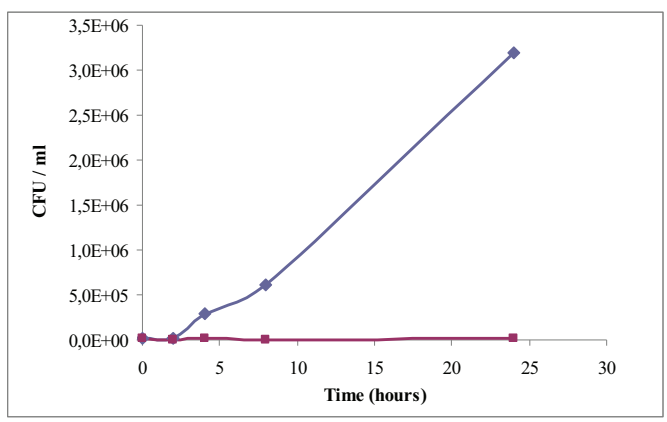

Figure 4: Development of Staphylococcus aureus vs time over polyester textiles without (blue) and with (red) NPsAg°

4. Conclusions

The results of this work show that the layer by layer technique allows a consistent and reproducible preparation of polyester textiles with microbicidal or bacteriostatic properties suitable for use in medical care products. It was also proved that a uniform nanoparticle distribution over fibers surface is achievable by the *in situ* chemical reduction of a nanosilver precursor, and that the concentration of silver thus obtained is enough to warrant a significant antimicrobial activity against *Staphylococcus aureus*, which was chosen as a model microorganism taking into consideration its widespread distribution in most kinds of environment, and specifically at medical facilities. Furthermore the uniform size (30 nm average) and cuasispherical morphology of nanoparticles allow a nearly optimal surface / volume ratio and a reasonable slow release of Ag+ so that the bacteriostatic effect is quite constant with time, as can be seen from figure 4.

Further work is needed in order to shorten processing times, so that the technique may be more commercially competitive. A complementary line of work related to the same objective should be the implementation of standard cleansing tests in order to assess silver retention on the fibers, in order to optimize the ecological footprint of the process.

Acknowledgements

This work was funded jointly by Nanotek S.A. and a grant from Agencia de Promoción Científica y Tecnológica (Argentina). The collaboration in SEM analysis of Centro de Microscopia Aplicada (CMA) from Universidad de Buenos Aires (UBA), is also acknowledged.

References

Castellano J.J.,. Shafii S.M, Ko F., Donate G., Wright T.E., Mannari R.J., Payne W.G., Smith D.J., Robson M.C.. 2007. Comparative evaluation of silver-containing antimicrobial dressings and drugs. Int. Wound J.;4:114–122.

Decher G., 1997. Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites, Science, 277, (5330), 1232-1237.

Decher G., Hong J., Schmitt J., 1992. Buildup of ultrathin multilayer films by a self-assembly process:III. Consecutively alternating adsorption of anionic and cationic polyelectrolytes on charged surfaces, Thin Solid Films, 210, (1-2), 831-835.

Dong, H., Wang, D., Sun, G., Hinestroza, J., 2008. Assembly of Metal Nanoparticles on Electrospun Nylon 6 Nanofibers by Control of Interfacial Hydrogen Bonding Interactions, Chemistry of Materials, 20, 21, 6627-6632.

Duran N., Marcarto P.D., De Souza G.I.H., Alves O.L., Esposito E., 2007. Antibacterial effect of silver nanoparticles produced by fungal process on textile fabrics and their effluent treatment, J. Biomedical Nanotechnology; 3:203-8.

Kim J.S., Kuk E., Yu K.N., Kim J.H., Park S.J., Lee H.J., 2007. Antimicrobial effects of silver nanoparticles, Nanomed. Nanotechnol Biol Med; 3:95-101.

Lansdown A.B.G. 2006. “Silver in Health Care: antimicrobial effects and safety in use; Biofunctional textiles and the skin”, Ed. Hipler, Elsner, Suiza.

Morones J.R., Elechiguerra J.L., Camacho A., Ramirez J.T., 2005. The bactericidal effect of silver nanoparticles. Nanotechnology;16:2346–53.

Rubner M., Shiratori S., 2000. pH-Dependent Thickness Behavior of Sequentially Adsorbed Layers of Weak Polyelectrolytes Macromolecules, 33, 4213 – 4219.